

Supporting Information:

Unprecedented 30 K Hysteresis across Switchable Dielectric and Magnetic Properties in a Bright Luminescent Organic-Inorganic Halide (CH₆N₃)₂MnCl₄

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TGA Curve

The thermogravimetric analysis has been carried out under nitrogen atmosphere. The compound starts decomposing above 480 K.

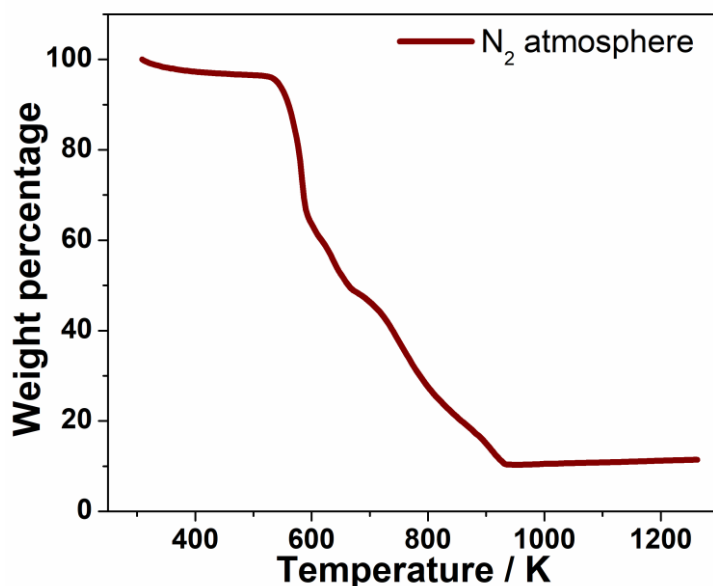


Figure S1 Thermogravimetric analysis data of **1**.

Table S1 Structural Refinement Details:

Parameters	HTP	LTP
Empirical formula	C ₂ H ₁₂ Cl ₄ MnN ₆	C ₂ H ₁₂ Cl ₄ MnN ₆
Formula weight (g/mol)	316.92	316.92
Temperature (K)	295	150
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions (Å)	<i>a</i> = 8.6611(4), <i>α</i> = 90.00° <i>b</i> = 27.0793(14), <i>β</i> = 93.237(4)° <i>c</i> = 15.6284(7), <i>γ</i> = 90.00°	<i>a</i> = 8.6227(5), <i>α</i> = 90.00° <i>b</i> = 27.0625(12), <i>β</i> = 90.00° <i>c</i> = 15.4303(7), <i>γ</i> = 90.00°
Volume (Å ³)	3659.6 (3)	3600.7 (3)
Z	12	12
Calculated density (g/cm ³)	1.726	1.754
Absorption coefficient (mm ⁻¹)	1.928	1.960
F(000)	1908	1908
Crystal dimension (mm ³)	0.17 x 0.15 x 0.32	0.17 x 0.15 x 0.32
Reflections collected	14809	9405
Independent reflections	7417 (<i>R</i> _{int} = 0.0687)	4129 (<i>R</i> _{int} = 0.0830)
Completeness to <i>θ</i> = 26.44°	99%	99.7%
Number of parameters	374	353
Goodness-of-fit	1.029	1.029
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> _{obs} = 0.0597, <i>wR</i> _{obs} = 0.1207	<i>R</i> _{obs} = 0.0664, <i>wR</i> _{obs} = 0.1466
<i>R</i> indices [all data]	<i>R</i> _{all} = 0.0965, <i>wR</i> _{all} = 0.1454	<i>R</i> _{all} = 0.0851, <i>wR</i> _{all} = 0.1618
CCDC number	1891611	1891612

Determination of thermal expansion coefficients:

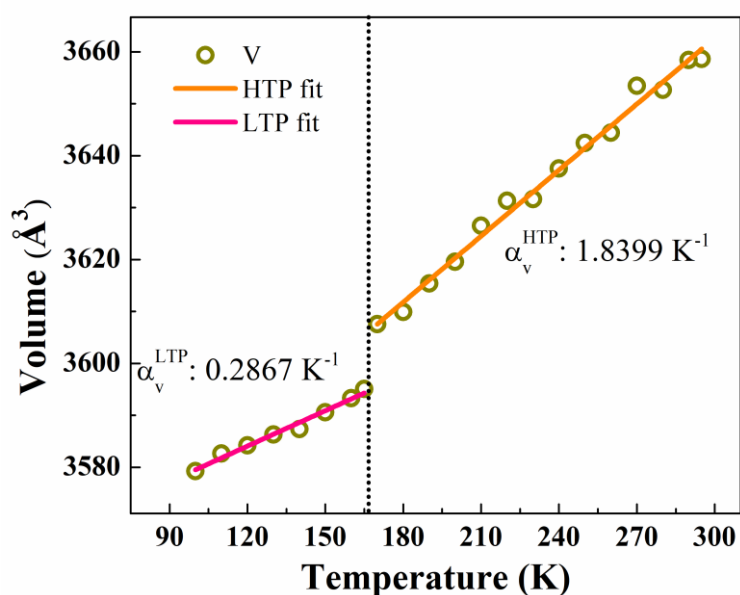


Fig. S2 Volumetric expansion coefficients calculated at both side of SPT from SCXRD.

Table S2 Bond Distances in $(\text{Mn}_3\text{Cl}_{12})^{6-}$ octahedral trimer at 295 K and 150 K:

295 K		150 K	
Bond Label	Bond distance (Å)	Bond Label	Bond distance (Å)
Mn(1)-Cl(1)	2.4689(16)	Mn(1)-Cl(1)	2.4633(3)
Mn(1)-Cl(2)	2.4598(18)	Mn(1)-Cl(2)	2.4643(3)
Mn(1)-Cl(3)	2.4730(17)	Mn(1)-Cl(3)	2.4713(3)
Mn(1)-Cl(4)	2.6654(15)	Mn(1)-Cl(4)	2.6563(3)
Mn(1)-Cl(5)	2.6962(15)	Mn(1)-Cl(5)	2.6113(3)
Mn(1)-Cl(6)	2.6079(15)	Mn(1)-Cl(6)	2.7143(3)
Mn(2)-Cl(4)	2.5659(16)	Mn(2)-Cl(4)	2.5653(3)
Mn(2)-Cl(5)	2.5617(15)	Mn(2)-Cl(5)	2.4953(3)
Mn(2)-Cl(6)	2.5021(13)	Mn(2)-Cl(6)	2.5623(3)
Mn(2)-Cl(7)	2.5286(15)	Mn(2)-Cl(7)	2.5183(3)
Mn(2)-Cl(8)	2.5253(15)	Mn(2)-Cl(8)	2.5243(3)
Mn(2)-Cl(9)	2.5375(13)	Mn(2)-Cl(9)	2.5373(3)
Mn(3)-Cl(7)	2.6717(15)	Mn(3)-Cl(7)	2.6733(3)
Mn(3)-Cl(8)	2.6523(15)	Mn(3)-Cl(8)	2.6463(3)
Mn(3)-Cl(9)	2.6568(15)	Mn(3)-Cl(9)	2.6583(3)
Mn(3)-Cl(10)	2.4750(17)	Mn(3)-Cl(10)	2.4503(3)
Mn(3)-Cl(11)	2.4647(17)	Mn(3)-Cl(11)	2.4593(3)
Mn(3)-Cl(12)	2.4560(15)	Mn(3)-Cl(12)	2.4963(3)

Thermal Properties

Background corrected DSC data for enthalpy calculations.

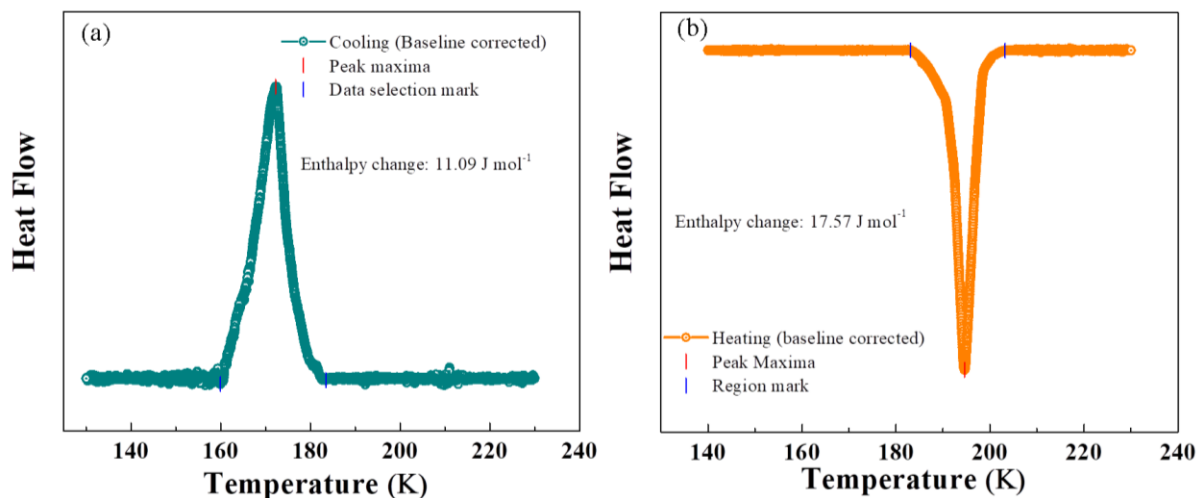


Fig. S3 Background subtracted DSC data (a) Heating and (b) cooling for enthalpy calculations.

Magnetic Properties

Curie-Weiss fitting in higher temperature region gives Curie constant $C = 3.28 \text{ emu} \cdot \text{mol}^{-1} \cdot \text{Oe}^{-1}$ with temperature intercept $\theta = -28.4 \text{ K}$. The negative value of θ along with the sigmoidal dependence of magnetization on magnetic field as recorded at 1.8 K indicate presence of antiferromagnetic interactions between spins at manganese sites.

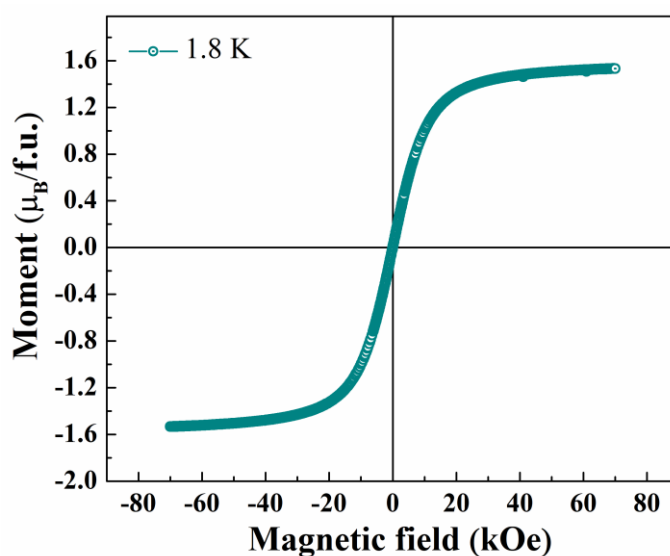


Fig. S4 Moment vs Magnetic field measured at 1.8 K.

Low temperature Photoluminescence

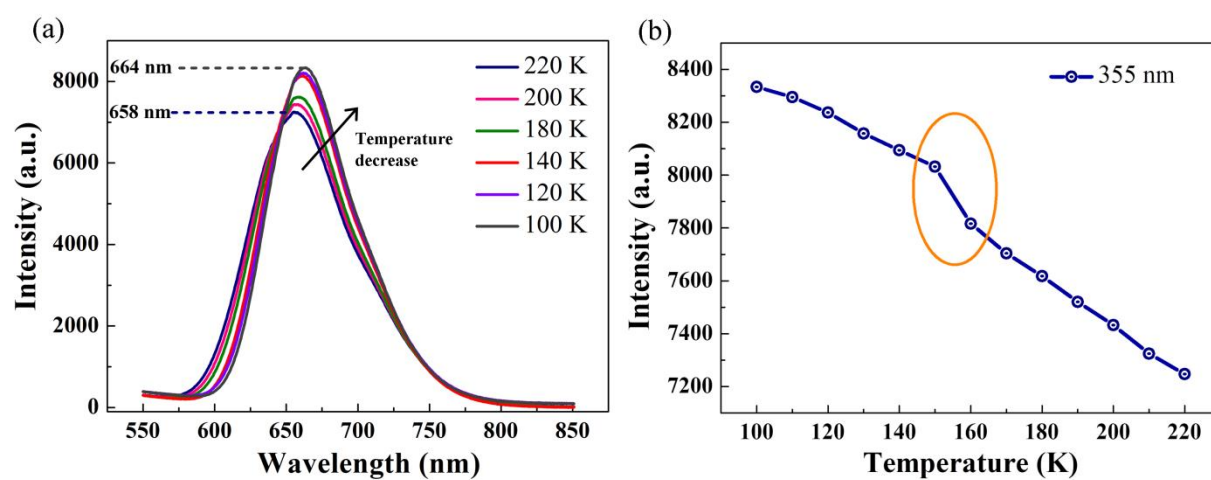


Fig. S5 (a) Emission spectra of recorded while cooling. Excitation wavelength was 355 nm, (b) Photoluminescence maxima plotted against temperature. The step-like change in switching near phase transition temperature can be observed.